INVESTIGATION OF THE ENVIRONMENTAL DISTRIBUTION AND ARCTIC TRANSPORT OF PERFLUOROOCTANOATE THROUGH THE APPLICATION OF A GLOBAL MASS BALANCE MODEL

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Introduction

Perfluorocarboxylates [F(CF2)nCO2H, n ≥ 7; PFCAs] and their potential precursors are of increasing scientific and regulatory interest because they are highly persistent in the environment and have been found globally in wildlife and in humans[1-4]. A congener of particular importance and extensive study is Perfluorooctanoic acid (PFOA) which is a weak acid (pK_a values generally between 2.5 to 2.8) indicating that both the anionic and protonated forms are present in the environment[5]. However, at typical environmental pH range of 5 to 8, >99% of the molecules will be ionized, resulting in environmental fate behavior that is dominated by the properties of the anion (Perfluorooctanoate or PFO).

A recent atmospheric modelling study indicated that approximately 0.4 tonnes/year of PFOA may be deposited to the Arctic from the global emission, distribution and degradation of 8-2 fluorotelomer alcohol[6]. However, PFO is highly water soluble and persistent and may possess an even higher potential for long-range ocean transport to the Arctic. Previous calculations of the importance of ocean water transport of PFO to the Arctic were simplistic[7]. Here, we undertake a more mechanistic investigation of global fate, ocean water transport to the Arctic and long-term trends in fluxes and concentrations of PFO using a global distribution model (GloboPOP). It is worth emphasizing to avoid confusion that we only model the fate of the anion (PFO) and not the protonated form. The model is evaluated against current monitoring data, and applied to forecast the effects of substantial reductions in the direct sources of PFCAs to the environment that have been committed to by industry.

Materials and Methods

Model: Globo-POP is a non-steady state, multi-compartment mass balance model designed to describe the global fate of persistent organic pollutants (POPs). The model has been previously used and evaluated for alpha-hexachlorocyclohexane (α-HCH) and polychlorinated biphenyls[8-9]. It describes the global environmental fate of organic chemicals through a series of latitudinal or climatic zones, each of which is further divided into a set of discrete well-mixed compartments. The model describes transfer of chemical between the compartments of one climatic zone, and transport from one latitudinal band to another through the meridional movement of atmosphere and surface ocean. As inputs the model requires partitioning properties and degradation properties of the simulated chemical, as well as historical emission estimates on a global scale. The model calculates amounts and concentrations in each compartment and fluxes between them as a function of time.

The model was shown to perform satisfactorily in its previous application to α-HCH, which undergoes both atmospheric and ocean transport to the Arctic. Thus, a series of simulations were conducted assuming minimum and maximum values for key PFOA physical-chemical properties and emission levels as well as varying mode of entry. All environmental inputs in Globo-POP were the default values.

Emission estimates: The model requires spatially-explicit, media-specific and multi-year PFOA emissions in order to undertake global fate modelling calculations. The current work builds up on a recently published study where several PFOA sources were identified and emission loadings for 1950-2004 were documented[7]. Minor refinements to the emission estimation methodology were made to account for information from more recent literature studies. Furthermore, future emissions for 2005–2050 were projected based on industry's commitments to substantially reduce emissions[7]. According to our calculations, the projected cumulative emissions after 2005

are expected to decline by more than a factor of 7 (360-710t) compared to the respective between 1950 and 2004 (2700-5800t), whilst a total of five PFOA sources are expected to be completely eliminated by 2005.

An additionally novelty of the current study, as well as an important model input, is the quantification of media-specific emissions to air, water and land for each of the 13 identified emission sources. This information originated from published literature studies, technical and industry reports as well as from the Unites States Environmental Protection Agency Dockets. The influence of the mode of entry on model output was investigated by conducting simulations using the projected release estimates (average emission distribution of 66%, 21% and 13% for air, water and land respectively) and by assuming emissions of 100% to air, water and soil. In all calculations it was assumed that the compartmental distribution remained unchanged with time. Finally, we assumed that the majority (90%) of PFO emission occurs in the model's northern temperate zone, with 5% in the northern boreal and 5% in the northern subtropic zone. These emissions were proposed to be constant throughout the year; that is, it was assumed that there is no seasonality in the intensity of emissions. Only direct emissions of PFO from manufacture and use were included in the model simulations, which is by far the majority (80%)[7]. Indirect sources such as precursors, which we estimate to be a minor source of PFO(A), were not included in the modelling simulations because of complications in modelling the transport and degradation pathways of these compounds.[6]

Degradation: Under a wide range of environmental conditions PFOA has been found to be stable with little or no apparent abiotic or biotic degradation, with limited thermal and photochemical degradation under extreme conditions[10-11]. As an upper bound on the rate of degradation, a loss of 1% per year was assumed (corresponding to a half-life of 69 years), with an annual loss 0.01% assumed as the lower boundary on the rate of degradation.

Physical-chemical properties: The model also requires information about important properties such as vapour pressure, water solubility, air-water, K_{AW}, and organic carbon-water, K_{OC}, partition coefficients. Available min and max values from the literature were selected.

Results and discussion

Model output and comparison with monitoring data: Predicted concentrations in surface ocean waters for 2005 ranged from 30-95 pg/L and 180-550 pg/L in the North Polar and Northern Temperate zones respectively, i.e. only a factor of approximately three between minimum and maximum estimates in each zone. The differences between min and max estimates are primarily explained by the difference in emission levels, with the model output being less sensitive to K_{OC} and degradation variations. Additionally, the mode of entry had only a minor influence on model output, which suggests that uncertainties associated with release estimates from various sources are of low importance in the context of global-scale fate modelling.

Modelled PFO concentrations in ocean waters were subsequently compared with observed environmental levels from a recent study[12]. Although the number of samples was limited, model predictions agreed quite well with the monitoring data for the North and Mid-Atlantic Ocean, which ranged from 100-440 pg/L. Predicted concentrations were higher than measured in the Pacific Ocean (15-140 pg/L), however, this may result from the coarse spatial resolution of the model in relation to the location and discharge pathways of emission sources. The reconciliation between observed and model-generated levels suggests that emissions (at least to surface waters) are reasonably accounted for, and that the dominant fate processes (including degradation rates) are in accord with model predictions. Furthermore, once a reasonable model evaluation has been demonstrated, future changes in emission scenarios can be translated into projected changes in environmental concentrations with increased confidence.

Future trends: The model was further used to forecast concentrations to the year 2050. Figure 1 shows the change in concentration in the ocean water in the Northern Hemisphere for the period 1950-2050 assuming maximum emission levels (to 2004), a mixed mode of entry, negligible degradation and a minimum K_{OC} value. It is interesting to observe that ocean water concentrations in the Northern Polar zone of the model were estimated to have increased steadily from commencement of emissions in 1951 until the present day. The estimated doubling time of ocean water concentrations in the Northern Polar zone of the model between 1975 and 2005 of

approximately 8-10 years compares very favourably with estimated doubling times of PFO in Arctic biota of between 7 and 14 years[13].
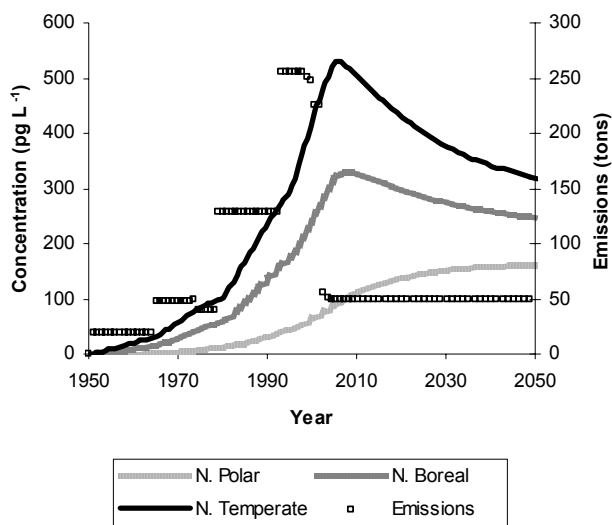

Figure 1. Illustrative long-term simulation of PFO in Northern Hemispheric Oceans.

After 2005, in the Northern Temperate and Northern Boreal zones of the model, ocean water concentrations are estimated to decline as a result of emission reductions, although there is a time lag of roughly 5 years before any decline in ocean water concentration emerges. Despite projected emission reductions, concentrations in the Northern Polar zone of the model are estimated to continue to increase during the entire period of the model simulation. This pattern is a result of the time required for extremely persistent chemicals such as PFO to redistribute throughout the oceans. These results have obvious implications for exposure of Arctic wildlife. If concentrations in the primary exposure media (i.e. surface water) continue to increase it follows that concentrations in wildlife would also continue to increase long after direct emissions have been drastically reduced or even eliminated.

Ocean water fluxes of PFO to the Arctic: The model was finally used to determine the net ocean transport flux of PFO to the Arctic (Figure 2).
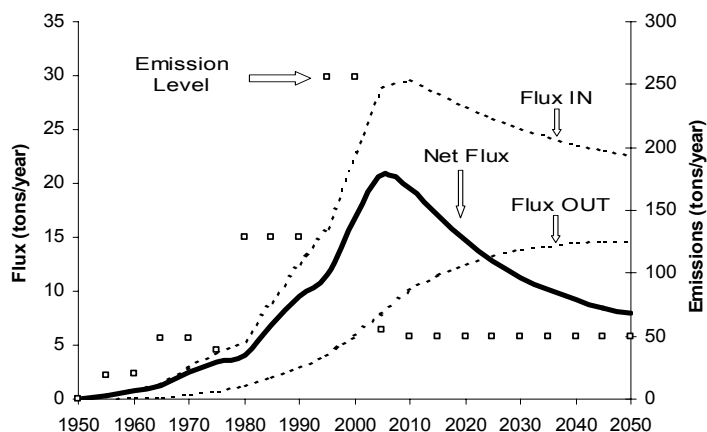

Figure 2. Illustrative time trend of flux of PFO to North Polar Zone.

It can be observed that depending on the scenario considered, a net flux of approximately 9-23 tonnes/year for PFO was estimated to flow into the Arctic in 2005, which is in agreement with a previously published estimate[7]. The time trend of estimated net flux into the Arctic followed the same pattern as the emission levels and increased from less than 1 ton/year in the 1950s to levels 20-fold higher by the year 2005. It is also noteworthy that even the lower bound of the amount estimated to flow into the Arctic via ocean water transport in 2005 is significantly higher than the amount estimated to be deposited as a result of the global emission, distribution and degradation of the 8-2- fluorotelomer alcohol[6].

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